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# Self-affine and mound roughness effects on the double-layer charge capacitance

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In this article, we investigate the influence of self-affine and mound roughness on the charge capacitance of double layers. The influence of self-affine roughness is more significant for small roughness exponents ($H<0.5$) and/or large roughness ratios $w/\xi$, as well as small charge and counter charge separations in electrolyte plasma as described by the Debye length $\lambda_D(<\xi)$. On the other hand, mound roughness has a more complex influence on the charge capacitance, when the system correlation length $\zeta$ is larger than the average mound separation $\lambda$. In this case, the charge capacitance oscillates as a function of the parameters $\lambda$ and $\zeta$ before it approaches the Gouy–Chapman [G. Gouy, J. Phys. (Paris) **9**, 457 (1910); D. L. Chapman, Philos. Mag. **25**, 475 (1913)] asymptotic limit for smooth interfaces. Furthermore, the oscillation magnitude is larger for relatively small Debye lengths $\lambda_D(<\zeta,\lambda)$. © *2002 American Institute of Physics.*
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## I. INTRODUCTION

Many important constructions in electrochemistry,[1] colloid science,[2] biophysics,[3] and semiconductor technology,[4] are based on the Gouy–Chapman (GC)[5] theory of electrolyte plasma near a flat charged wall. For low voltages, the GC theory yields a space-charge capacitance $C_{\rm GC}=\epsilon S/4\pi\lambda_D$ with $\epsilon$ the solvent dielectric constant, $S$ is the area of the flat interface, and $\lambda_D$ is the Gouy or Debye length.[6] The latter is a measure of the separation of charge and counter charge in the electrolyte plasma.

For a long period in electrochemistry, studies were performed on a liquid mercury drop electrode, and later on GaTi, Ga, and InGa electrodes.[7] Studies on solid electrodes (i.e., Cd, Bi, Cu, and Pb) revealed problems that were associated with metal/electrolyte interface roughness.[8] We have to stress that one can not consider metal/electrolyte interface roughness by simply replacing surface area $S$ by $RS$ in the equation for $C_{\rm GC}$, where $R$ is the ratio of the true surface to the apparent flat crosssection area $S$. This is because the characteristic roughness length scale $L$ can compete with characteristic length scales of the system such as the Debye length $\lambda_D$. This competition will lead to a different functional dependence of the charge capacitance on electrode potential and electrolyte concentration.[9] For short Debye lengths ($\lambda_D \ll L$), the charge capacitance is expected to be given by $C=\epsilon RS/4\pi\lambda_D$. However, for large Debye lengths ($\lambda_D \gg L$), the charge capacitance $C$ will approach $C_{\rm GC}$, since the interface roughness does not have any influence on $C$.[9]

Application of the theory by Daikhin *et al.*[9] was performed earlier for electric double layers with Bi, Sb, and Cd electrodes.[10] The deviations between experimental and theoretical curves of the roughness function versus inverse Debye length $\lambda_D$ were explained in terms of the influence of energetic inhomogeneity of polycrystalline surfaces.[10] Furthermore, extension of the theory to the case of the nonlinear Poisson–Boltzmann theory was performed by Daikhin *et al.*[11] and Lust *et al.*[12] who successfully explained data for Cd rough electrodes.

In the original work by Daikhin *et al.*,[9] which is based on the linear Poisson–Boltzmann theory, the case of intermediate Debye lengths $\lambda_D$ was explored in the case of weak roughness. The various examples of rough interfaces included sinusoidal corrugation, Gaussian roughness, and some limiting cases of self-affine roughness for significantly large roughness exponents $H$ ($>0.5$).[9] The roughness exponent $H$ characterizes the degree of surface irregularity at short length scales ($<\xi$, where $\xi$ is the lateral roughness correlation length) so as $H$ becomes smaller, the interface becomes more irregular.

In this work, we present an extension of the former studies to the case of self-affine roughness with roughness exponents $H<0.5$, by properly setting the limits of the perturbative approach for weak electrode roughness.[9] Moreover, we will extend these studies to the case of mound roughness, which is observed during unstable film growth.[13,14] In many cases, the film growth front is rough because multilayer step structures are formed during growth,[13,14] or alternatively noise induced roughening can lead to the formation of self-affine rough morphologies.[15,16] In the first case, the existence of an asymmetric step-edge diffusion barrier or Schwoebel barrier inhibits the downhill diffusion of incoming atoms, leading to the creation of large structures in the form of mounds.[13,14]

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## II. CHARGE CAPACITANCE THEORY

In this article, we will assume that the rough metal/electrolyte interface can be described by a single valued random function of the in-plane position vector $r=(x,y)$ $z=h(r)$ with the average flat interface area at $z=0$ ($\langle h(r)\rangle=0$). The rough interface is assumed to be held at potential $\Phi_0$. For low electrostatic potential $\Phi(r)$ ($\langle k_BT/e\rangle$), the problem simplifies to the solution of the linear Poisson–Boltzmann equation $\nabla^2\Phi-\lambda_D^{-2}\Phi=0$ with boundary conditions $\Phi[x,y,z=h(x,y)]=\Phi_0$ and $\Phi(x,y,z\rightarrow+\infty)=0$.[9] Furthermore, it is assumed that the electrolyte occupies the half-space $z>0$. In the limit of weak roughness ($|\nabla h|\ll 1$ and $h\ll\lambda_D$), the charge capacitance $C$ is given by the expression[9]

$$\frac{C}{C_{\rm GC}}=1+\frac{1}{\lambda_D}\int_{0<q<Q_c}[\sqrt{(\lambda_D^{-2}+q^2)}-\lambda_D^{-1}]\times\langle|h(q)|^2\rangle\frac{d^2q}{(2\pi)^2},\tag{1}$$

where $\langle|h(q)|^2\rangle$ is the metal/electrolyte interface roughness spectrum.

The requirement of weak roughness ($|\nabla h|\ll 1$ and $h\ll\lambda_D$) for the validity of Eq. (1) can be reformulated more precisely by the requirement that the average local interface slope to be small or $\rho_{\rm rms}=\sqrt{\langle|\nabla h|^2\rangle}\ll 1$, and $w/\lambda_D\ll 1$ with $w=\sqrt{\langle h^2\rangle}$ the saturated root-mean-square (rms) roughness amplitude. The average local slope $\rho_{\rm rms}$ is given in terms of the roughness spectrum $\langle|h(q)|^2\rangle$ by the expression

$$\rho_{\rm rms}=\left\{\int_{0<q<Q_c}q^2\langle|h(q)|^2\rangle\frac{d^2q}{(2\pi)^2}\right\}^{1/2},\tag{2}$$

where $Q_c=\pi/c$ with $c$ a lower roughness cutoff of the order of atomic dimensions.

## III. ROUGHNESS MODELS

In this section, we will consider models for the roughness spectrum $\langle|h(q)|^2\rangle$ which are necessary for the calculation of the charge capacitance in terms of Eq. (1).

### A. Self-affine roughness

Any physical self-affine morphology is characterized by the finite correlation length $\xi$, the rms roughness amplitude $w$, and the roughness exponent $H$ ($0<H<1$) which is a measure of the degree of surface irregularity.[15] Small values of $H$ ($\sim 0$) characterize extremely jagged or irregular surfaces, while large values $H(\sim 1)$ characterize surfaces with smooth hills and valleys.[15] For self-affine fractals, the roughness spectrum $\langle|h(q)|^2\rangle$ is characterized by the power-law scaling behavior $\langle|h(q)|^2\rangle\propto q^{-2-2H}$ if $q\xi\gg 1$, and $\langle|h(q)|^2\rangle\propto$ constant if $q\xi\ll 1$.[15] This scaling behavior is satisfied by the simple Lorentzian model[16]

$$\langle|h(q)|^2\rangle=\frac{2\pi w^2\xi^2}{(1+aq^2\xi^2)^{1+H}}\tag{3}$$

with $a=(1/2H)[1-(1+aQ_c^2\xi^2)^{-H}]$ if $0<H<1$, and $a=1/2\ln(1+aQ_c^2\xi^2)$ if $H=0$.

### B. Mound roughness

Mound rough surfaces have been described in the past by the interface width $w$, the system correlation length $\zeta$ which determines how randomly the mounds are distributed on the surface, and the average mound separation $\lambda$.[14] This rough morphology (which effectively corresponds to roughness exponent $H=1$) can be described in Fourier space by the model[14]

$$\langle|h(q)|^2\rangle=\pi w^2\zeta^2e^{-(4\pi^2+q^2\lambda^2)(\zeta^2/4\lambda^2)}I_0(\pi q\zeta^2/\lambda),\tag{4}$$

with $I_0(x)$ as the modified Bessel function of first kind and zero order. Note that for $\zeta\geqslant\lambda$ (strong Schwoebel barrier effect during roughness growth), a characteristic satellite ring at $q=2\pi/\lambda$ of the power spectrum $\langle|h(q)|^2\rangle$ occurs.[14]

## IV. RESULTS AND DISCUSSION

In general, the charge capacitance will have a simple dependence on the roughness amplitude $w$, since $\langle|h(q)|^2\rangle\propto w^2$, while a more complex dependence will arise from the roughness parameters $H$ and $\xi$ for self-affine roughness, or from the roughness parameters $\lambda$ and $\zeta$ for mound roughness. Our calculations were performed for roughness amplitude $w=1$ nm and Debye lengths $\lambda_D$ such that $w/\lambda_D\leqslant 0.1$, a lower roughness cutoff $c=0.3$ nm, and local interface slopes $\rho_{\rm rms}=\sqrt{\langle|\nabla h|^2\rangle}<1$. We have to point out that the lower roughness cutoff ($c=0.3$ nm in present calculations) corresponds to a typical lattice constant for metals. However, a lower value might be necessary for real physical systems (depending on the material), since the actual smallest step height might be smaller than the lattice constant.

From the self-affine roughness model given by Eq. (3), we obtain the following analytic expression for the average local slope

$$\rho_{\rm rms}^{\rm self\text{-}affine}=\frac{w}{\sqrt{2}a\xi}\left\{\frac{1}{1-H}[(1+aQ_c^2\xi^2)^{1-H}-1]-2a\right\}^{1/2}.\tag{5}$$

For mound roughness, if we extend the integration in Eq. (2) to infinity, we obtain for the average local slope the approximate result

$$\rho_{\rm rms}^{\rm mound}\approx\frac{w}{\sqrt{2}}\left[\frac{1}{\zeta^2}+\frac{\pi^2}{\lambda^2}\right]^{1/2}\tag{6}$$

Figure 1(a) shows the dependence of the local slope versus the roughness ratio $w/\xi$ for the case of self-affine roughness. Clearly, the roughness exponent $H$ strongly influences the local slope. This result implies that Eq. (1) for the charge capacitance will be valid if $H$ decreases below 0.5 for lower ratio $w/\xi$. For logarithmic roughness ($H=0$), Eq. (1) is only valid for ratios $w/\xi\ll 1$. On the other hand for mound roughness (corresponding to $H=1$[14]), the validity of Eq. (1) is less restricted for the roughness parameters used in Fig. 1(b).

Figure 2 indicates that the charge capacitance $C$ increases with decreasing Debye length $\lambda_D$ which is consistent for small roughness exponents $H<0.3$ as well as large ones $H>0.5$, based on the simple model for the roughness spectrum given by Eq. (3). One should note that with decreasing

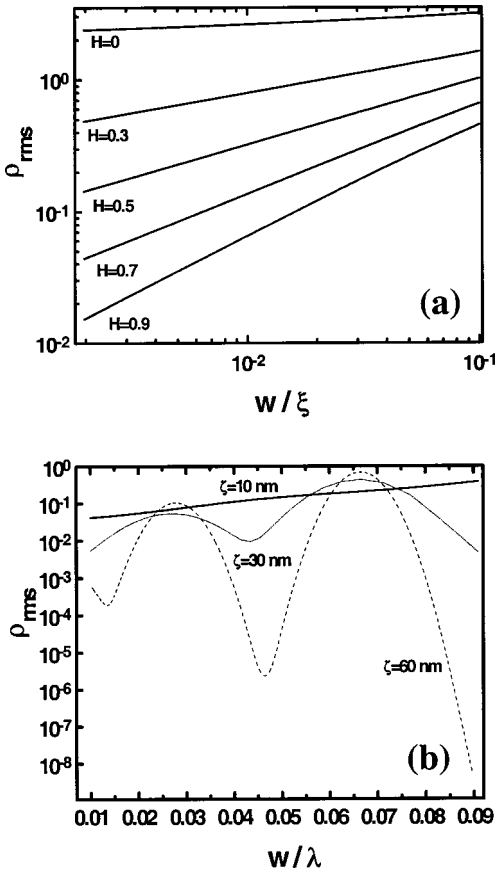


FIG. 1. (a) Local slope for self-affine roughness vs the roughness ratio $w/\xi$ and various roughness exponents $H$ as indicated. (b) Local slope for mound roughness vs roughness ratio $w/\lambda$ for various system correlation lengths $\zeta$ as indicated.

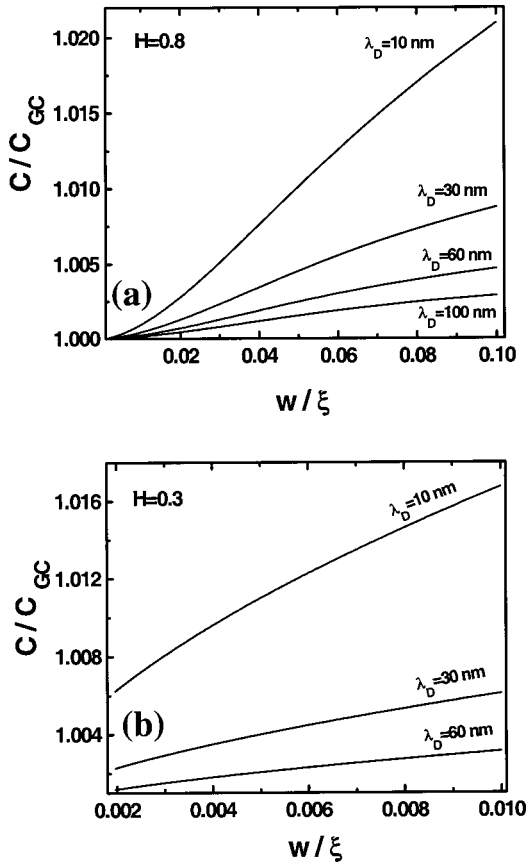


FIG. 2. Capacitance ratio $C/C_{GC}$ vs roughness ratio $w/\xi$ for various Debye lengths and (a) $H=0.8$ and (b) $H=0.3$.

roughness exponent $H$ (increasing roughness irregularity at short lateral wavelengths $<\xi$), the charge capacitance strongly increases even for very small long wavelength roughness ratios $w/\xi$ ($\leqslant 0.01$). Figure 3 shows the dependence of the charge capacitance on the length scale ratio $\lambda_D/\xi$ for various roughness exponents $H$. Clearly, the effect of the roughness exponent $H$ on the charge capacitance is significant for relatively short Debye lengths $\lambda_D<\xi$, when the roughness exponent $H$ remains significantly small ($H<0.5$).

Although the situation for self-affine roughness is rather straightforward, the influence of mound roughness appears to be more complex. Figure 4(a) indicates that by increasing Debye length $\lambda_D$, the capacitance magnitude decreases towards the GC prediction for flat interfaces. The capacitance decrement takes place in a oscillating manner with increasing average mound separation $\lambda$. The oscillations are higher in magnitude if the average mound separation $\lambda$ is smaller than the system correlation length $\zeta$. Indeed, $\lambda<\zeta$ represents the case of significant Schowebel barriers during roughness growth.[11] The latter is also clearly observed in Fig. 4(b) where the charge capacitance strongly fluctuates from the GC prediction when $\lambda<\zeta$.

Figure 5 shows the direct dependence of the charge capacitance on the system correlation length $\zeta$. Due to the exponential dependence on $\zeta$ of Eq. (4), the charge capacitance will decrease with increasing $\zeta$ due to interface smoothing. However, at intermediate values which are comparable to the average mound separation $\lambda$ (and for relatively small $\lambda$), an oscillatory behavior develops as Fig. 5(a) indicates. These oscillations fade away with increasing Debye length $\lambda_D$, as is clearly shown in Fig. 5(b). The oscillations of the local slope (Fig. 1) and of the charge capacitance in Figs. 4 and 5 are related with the characteristic satellite ring at $q=2\pi/\lambda$ of the power spectrum $\langle|h(q)|^2\rangle$.[14] The latter yields upon integration the height–height correlation function $C(r)$

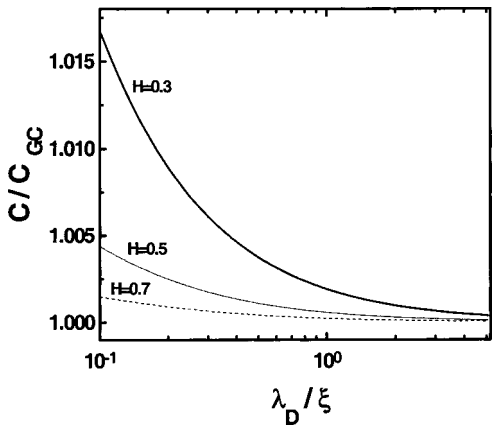


FIG. 3. Capacitance ratio $C/C_{GC}$ vs $\lambda_D/\xi$ for $\xi=100$ nm ($w/\xi\ll 1$), and various roughness exponents $H$.

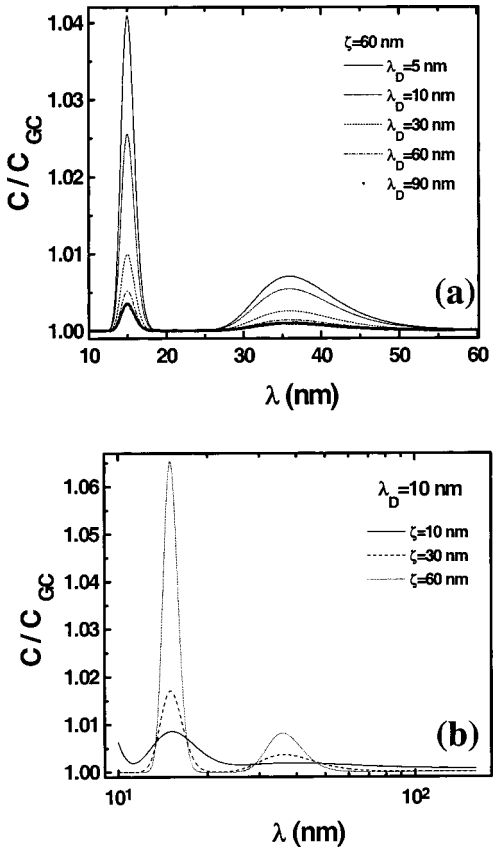


FIG. 4. (a) Capacitance ratio $C/C_{\mathrm{GC}}$ vs average mound separation $\lambda$ for $\zeta = 40$ nm, and various Debye lengths $\lambda_D$. (b) Capacitance ratio $C/C_{\mathrm{GC}}$ vs average mound separation $\lambda$ for a small Debye length $\lambda_D = 10$ nm, and various system correlation lengths $\zeta$.

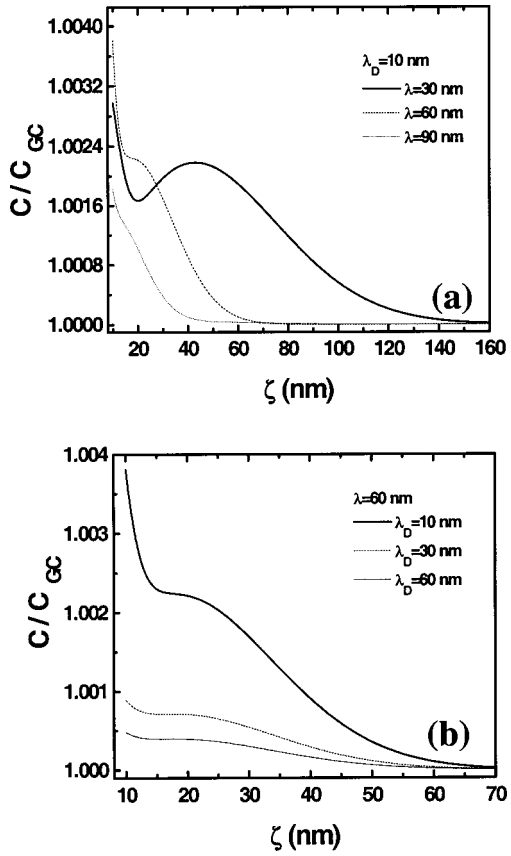


FIG. 5. (a) Capacitance ratio $C/C_{\mathrm{GC}}$ vs system correlation length $\zeta$ for various average mound separation $\lambda$ and Debye lengths $\lambda_D = 10$ nm. (b) Capacitance ratio $C/C_{\mathrm{GC}}$ vs system correlation length $\zeta$ for average mound separation $\lambda = 60$ nm and various Debye lengths $\lambda_D$.

$\times[\propto \int \langle |h(q)|^2 \rangle e^{-iqr} d^2r] = w^2 e^{-(r/\zeta)^2} J_0(2\pi r/\lambda)$ which exhibits similar oscillation behavior in real space due the presence of the zero-order Bessel function $J_0(x)$. For the local slope and thus for the charge capacitance, the oscillatory behavior is preserved if we keep the upper limit of integration $Q_c$ finite, due to the presence of the modified Bessel function $I_0(x)$ in Eq. (4).

## V. CONCLUSIONS

In summary, we have investigated the influence of self-affine and mound roughness on the charge capacitance of double layers. The criterion of the average local interface slope $\rho_{\mathrm{rms}} = \sqrt{\langle |\nabla h|^2 \rangle}$ (besides the requirement of low rms roughness amplitude $w < \lambda_D$) provides the necessary tool for the correct application of the perturbative approach in the limit of weak roughness. The influence of self-affine roughness is more significant for small roughness exponents ($H < 0.5$) and/or large roughness ratios $w/\xi$, as well as small Debye lengths $\lambda_D$ ($< \xi$). On the other hand, mound roughness has a more complex influence on the charge capacitance if the system correlation length $\zeta$ is larger than the average mound separation $\lambda$. In this case, the charge capacitance oscillates as a function of the parameters $\lambda$ and $\zeta$ before it approaches the GC asymptotic limit for smooth interfaces ($w/\zeta$ and $w/\lambda \ll 1$). Moreover, the oscillation magnitude is larger for smaller Debye lengths $\lambda_D$.

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